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Syntheses and Patterns of Changes in Structural Parameters of the New Quaternary Tellurides $EuRECuTe_3$ (RE = Ho, Tm, and Sc): Experiment and Theory

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Abstract: The layered orthorhombic quaternary tellurides EuRECuTe₃ (RE = Ho, Tm, Sc) with Cmcm symmetry were first synthesized. Single crystals of the compounds up to 500 µm in size were obtained by the halide-flux method at 1120 K from elements taken in a ratio of Eu/RE/Cu/Te = 1:1:1:3. In the series of compounds, the changes in lattice parameters were in the ranges a = 4.3129(3) - 4.2341(3) Å, b = 14.3150(9)-14.1562(9) Å, c = 11.2312(7)-10.8698(7) Å, V = 693.40(8)-651.52(7) Å³. In the structures, the cations Eu^{2+} , RE^{3+} (RE = Ho, Tm, Sc), and Cu^+ occupied independent crystallographic positions. The structures were built with distorted copper tetrahedra forming infinite chains [CuTe₄]^{7–} and octahedra $[RETe_6]^{9-}$ forming two-dimensional layers along the *a*-axis. These coordination polyhedra formed parallel two-dimensional layers $^{2}_{\infty} \{ [CuRETe_{3}]^{2-} \}$. Between the layers, along the *a*-axis, chains of europium trigonal prisms $[EuTe_6]^{10-}$ were located. Regularities in the variation of structural parameters and the degree of distortion of coordination polyhedra depending on the ionic radius of the rare-earth metal in the compounds $EuRECuCh_3$ (RE = Ho, Er, Tm, Lu, Sc; Ch = S, Se, Te) were established. It is shown that with a decrease in the ionic radius $r_i(RE^{3+})$ in the compounds $EuRECuTe_3$, the unit-cell volume, bond length d(RE-Te), distortion degree [CuTe₄]⁷⁻, and crystallographic compression of layers [RECuTe₃]²⁻ decreased. The distortion degree of tetrahedral polyhedra $[CuCh_4]^{7-}$, as well as the structural parameters in europium rare-earth copper tellurides EuRECuTe₃, were higher than in isostructural quaternary chalcogenides. Ab initio calculations of the crystalline structure, phonon spectrum, and elastic properties of compounds $EuRECuTe_3$ (RE = Ho, Tm, and Sc) ere conducted. The types and wave numbers of fundamental modes were determined, and the involvement of ions in IR and Raman modes was assessed. The calculated data of the crystal structure correlated well with the experimental results.

Keywords: quaternary europium copper tellurides; syntheses; crystal structure; DFT calculations; rare-earth metals

1. Introduction

Studying four-component tellurides opens up new perspectives for creating materials with unique properties and potential applications in various fields, including electronics, optics, and energy [1–6]. Understanding the influence of structural features on the properties of chalcogenide materials allows for the modification of the band gap width, electrical, and optical properties of the materials [7–15]. The presence of a large variety of coordination polyhedra and different ways of connecting them in tellurides creates conditions for the formation of layered or tunnel structures [6,9]. Layered tellurides of the



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). space group *Cmcm* demonstrate promising efficiency in solar energy conversion and are considered as prospective absorbers in solar cell structures, as well as thermoelectric materials [1-4]. It is assumed that in compounds of the space group Cmcm, such as MRECuTe₃ (M = d-element) with the structure type of KZrCuS₃, there is a covalently bonded sublattice $[RECuTe_3]^{2-}$, leading to improved electrical transport properties, and the M^{2+} cations induce low lattice thermal conductivity [1,2]. Tellurides of the space group *Cmcm* contain non-centrosymmetric tetrahedral coordination polyhedra [16], allowing them to be used in nonlinear optical devices as photon media [17,18]. In the EuRECuCh₃ structures, a tetrahedral structural motif is clearly visible in the form of one-dimensional chains of distorted $[CuCh_3]^{5-}$ [18–26] tetrahedra. Compounds BaRECuCh₃ (Ch = chalcogen) are used as hole transport materials in solar cells, significantly increasing the efficiency of the solar cell (up to 45%) compared to a cell without this chalcogenide [1,27,28]. It was previously established that replacing the alkaline earth M^{2+} ions in the quaternary chalcogenides $MRECuCh_3$ with the Eu²⁺ cation makes it possible to narrow the band gap of the compound due to the presence of the 4f-5d transition in the Eu²⁺ ion [8]. Also, an increase in the chalcogen radius in the series $r_i(S^{2-}) > r_i(Se^{2-}) > r_i(Te^{2-})$ reduces the value of the band gap [7]. Thus, it is expected that the synthesis of EuRECuTe₃ compounds will make it possible in the future to obtain semiconductor materials with the bandgap value required for photovoltaic materials and use them as a photoanode in multilayer solar cells, improving charge separation as well as reducing the recombination of electrons and holes at the interface of the photoanode and electrolyte.

Experimental and theoretical studies of the sulfide series of europium compounds $EuRECuS_3$ were carried out for quite a long time from 1986 to 2021 [8,22–24,29], and similar studies of the selenide series $EuRECuSe_3$ were carried out from 2022 to 2024 [18,25,26]. Research has shown that the compounds are p-type semiconductors, low-temperature ferroand ferrimagnets, with a negative magnetization effect, high-temperature stability in an inert atmosphere, and polymorphism [8,16,18,22–26,29]. A decrease in incongruent melting temperatures and band gaps with changes in chalcogen has been established [8,24,26]. From the $EuRECuTe_3$ series of europium tellurides, only three have been obtained to date: $EuGdCuTe_3$ [20], $EuErCuTe_3$ [19], and $EuLuCuTe_3$ [20] (Figure 1). However, quaternary tellurides with alkaline earth elements $BaRECuTe_3$ (RE = Pr-Yb, Sc) [1,16,17,30,31] and $SrRECuTe_3$ (RE = Dy-Lu, Sc) [1,12,16] are described in detail in the literature. The smaller the ionic radius of the M^{2+} cation in the compounds $MRECuTe_3$, the fewer compounds will crystallize in the space group Cmcm [12]. The Eu^{2+} cation has a smaller ionic radius than the Sr^{2+} and Ba^{2+} cations [32]. It can be assumed that compounds $EuRECuTe_3$ (RE = Ho-Lu and Sc) will crystallize in the space group Cmcm.

For compounds EuTmCuTe₃ and EuScCuTe₃, the structure type of NaCuTiS₃ has been predicted [2], crystallizing in the space group *Pnma* [33]. According to DFT calculations using the PBE functional in this space group, the band gap widths of these compounds are 0.59 and 0.40 eV, respectively [2]. The structure of the orthorhombic crystal NaCuTiS₃ is characterized by distorted copper tetrahedra and titanium octahedra forming two-dimensional layers [CuTiS₃]⁻ along the *c*-axis [33]. Single-capped trigonal prisms of sodium are located between the layers. However, previously obtained scandium and thulium quaternary chalcogenides *MRECuCh*₃ (*M* = Eu [8,18,22,24,25], Sr [8,12,34–36], Ba [1,37–39]; *RE* = Sc, Tm; *Ch* = S, Se, Te) crystallize in the space group *Cmcm* with the KZrCuS₃-type structure. It is expected that compounds EuScCuTe₃ and EuTmCuTe₃ will crystallize in the same structure type and space group as compounds with isostructural composition [22,24,25,35–39].

There are no literature data on attempts to synthesize and establish the crystal structure of tellurides $EuRECuTe_3$ (RE = Ho, Tm, Yb, Sc). In this work, we first describe the single-crystal synthesis of $EuRECuTe_3$ (RE = Ho, Tm, and Sc), investigating their crystal structure both experimentally and using theoretical methods.



Figure 1. Structure field diagram of *MRE*CuTe₃ tellurides with M = Ba [1,16,17,30,31], Sr [1,12,16], Eu [19,20]. Description: color background corresponds to a defined structure type (space group *Pnma*—orange (Eu₂CuS₃); space group *Cmcm*—green (KZrCuS₃)). The black line delimits the regions of existence of the space groups *Pnma* and *Cmcm*.

2. Experimental

2.1. Materials

Ho (99.9%), Tm (99.9%), Yb (99.9%), Sc (99.9%), Eu (99.99%), Te (99.9%), Ar (99.99%), C₂H₂ (99.9%), and CsI (99.9%) were purchased from ChemPur (Karlsruhe, Germany). Cu (99.999%) was obtained from Aldrich (Milwaukee, WI, USA).

2.2. Synthesis

Single crystals of $EuRECuTe_3$ (RE = Ho, Tm, Sc) were synthesized from elements taken in a ratio of Cu/Eu/RE/Te = 1:1:1:3 with the addition of cesium iodide as a flux. Due to the rapid oxidizability of rare-earth metals by components of the air (oxygen, carbon dioxide, water vapor) at room temperature, the starting components were weighed in an inert atmosphere using a glovebox. A layer of amorphous carbon obtained by pyrolysis of acetylene was pre-applied to the inner walls of the silica ampoules. After filling the ampoules with the starting components, they were tightly sealed with a quick-release seal, removed from the glove box, connected to a vacuum pump, evacuated to a residual pressure of 2×10^{-3} mbar, sealed, and heated in a muffle furnace. The temperature in the furnace was raised from room temperature to 1120 K over 30 h with subsequent isothermal holding for 96 h. Cooling was carried out to 570 K over 140 h and to 300 K over 3 h. Residual flux from the sample was removed with demineralized water. The products were black needle-like crystals of EuRECuTe₃ (RE = Ho, Tm, Sc) up to 500 μ m in size (Figure 2). The obtained crystals were suitable for single crystal X-ray diffraction analysis. Unfortunately, it was not possible to obtain high-quality powder diffraction patterns, as copper compounds strongly absorb molybdenum radiation. The yield of tellurides was 10–15%, which did not allow for the experimental determination of the optical properties of the samples. Unfortunately, despite numerous attempts, we were unable to obtain the compound EuYbCuTe₃ using the flux method. The samples after synthesis contained single crystals of $Cu_{0.37}$ YbTe₂, EuTe, and YbTe. The phase of EuYbCuTe₃ was not found in the samples, possibly due to the weak oxidizing ability of tellurium interfering with the Yb⁰–3e⁻ \rightarrow Yb³⁺ redox reaction.



Figure 2. Photograph of EuHoCuTe₃ (**left**) and EuScCuTe₃ (**right**) crystals placed in a capillary for X-ray diffraction analysis.

2.3. X-ray Diffraction Analysis

The intensities from a single crystal of the Eu*RE*CuTe₃ (*RE* = Ho, Tm, Sc) were collected at 293(2) K using a SMART APEX II single-crystal diffractometer (Bruker AXS, Billerica, MA, USA) equipped with a CCD-detector, graphite monochromator, and Mo- K_{α} radiation source. The parameters of the unit cell were determined and refined for a set of 11,880 reflections. The parameters of the unit cell correspond to the orthorhombic crystal system. The space group *Cmcm* was determined from the statistical analysis of all intensities. Absorption corrections were applied using the SADABS program. The crystal structure was solved by direct methods using the SHELXS program and refined in an anisotropic approximation using the SHELXL program [40]. Structural investigations for the presence of missing symmetry elements were conducted using the PLATON program [41]. The crystallographic data are deposited in Cambridge Crystallographic Data Centre. The data can be downloaded from the site www.ccdc.cam.ac.uk/data_request/cif (accessed on 25 February 2024).

2.4. DFT Calculations

Calculations were performed at the theoretical level DFT by using hybrid functional B3LYP [42] that take into account non-local exchange at Hartree–Fock formalism. This approach is suitable for to compounds with ionic and covalent chemical bonds. We used CRYSTAL17 code [43]. The program is designed for modeling periodic compounds within the framework of the MO-LCAO approach. Stuttgart pseudopotentials ECP*n*MWB for Eu²⁺ and *RE*³⁺ cations were used [44]. Here, *n* is the number of electrons that replaces this pseudopotential. For Eu²⁺, *n* was equal Z–10, and for RE³⁺, *n* was equal Z–11 (Z is atomic number). For outer shells $5s^25p^6$ of rare-earth metal ions, which were involved in chemical bonds, attached basis sets of TZVP type were used [44]. For scandium and copper, we used all-electron basis sets «Sc_pob_TZVP_2012» and «Cu_86-4111(41D)G_doll_2000», available on the website of program CRYSTAL [43]. For tellurium, we used an all-electron basis set [45] also. Gaussian-type orbitals with exponents lower than 0.1 were cancelled from the basis sets. Self-consistent field was calculated with tolerance 10^{-9} a.u. Monkhorst-Pack grid used was $8 \times 8 \times 8$ k-points.

Optimization of the crystal structure was performed at first. After that, elastic constants and phonon spectrum were calculated for optimized crystal structure.

3. Results

3.1. Crystal Structures of the EuRECuTe₃ (RE = Ho, Tm, Sc)

In the series of europium tellurides $EuRECuTe_3$, only three orthorhombic compounds $EuRECuTe_3$ (RE = Gd [20], Er [19], Lu [20]) have been previously obtained using the halide flux method. The compound $EuGdCuTe_3$ [20] crystallizes in the space group *Pnma* in the structure type of Eu_2CuS_3 , while the compounds $EuErCuTe_3$ [19] and $EuLuCuTe_3$ [20] crystallize in the space group *Cmcm* in the structure type of KZrCuS_3. Single-crystal

	EuHoCuTe ₃	EuTmCuTe ₃	EuScCuTe ₃
Molecular weight (g/mol)	765.56	767.23	643.26
Space group		<i>Cmcm</i> (no. 63)	
Structure type		KZrCuS ₃	
Z		4	
a (Å)	4.3129(3)	4.3054(3)	4.2341(3)
b (Å)	14.3150(9)	14.3017(9)	14.1562(9)
<i>c</i> (Å)	11.2312(7)	11.1683(7)	10.8698(7)
V (Å ³)	693.40(8)	687.68(8)	651.52(7)
$\rho_{\rm cal} ({\rm g/cm^3})$	7.311	7.410	6.558
$\mu (\mathrm{mm}^{-1})$	35.512	37.203	26.781
Reflections measured	6492	6639	6286
Reflections independent	481	478	451
Reflections with $F_{o} > 4\sigma(F_{o})$	0.030	0.021	0.031
$ heta_{\max}$ (°)	27.44	27.48	27.53
<i>h</i> , <i>k</i> , <i>l</i> limits	$-5 \leq h \leq$	$5, -18 \le k \le 18, -14$	$l \leq l \leq 14$
$R_{\rm int}, R_{\sigma}$	0.109, 0.047	0.069, 0.024	0.065, 0.026
	Refinement results		
Number of refinement parameters		24	
R_1 with $F_0 > 4\sigma(F_0)$	0.030	0.021	0.024
wR_2	0.062	0.047	0.052
Goof	1.084	1.117	1.056
$\Delta \rho_{\rm max} ~({\rm e}/{\rm \AA}^3)$	1.857	1.431	1.503
$\Delta \rho_{\rm min} ~({\rm e}/{\rm \AA}^3)$	-1.783	-1.362	-1.467
Extinction coefficient, ε	0.00104(9)	0.00141(8)	0.0029(2)
CSD number	2261646	2261648	2354996

Table 1. Main parameters of processing and refinement of the EuRECuTe₃ (RE = Ho, Tm, Sc) samples.

The atomic coordinates, thermal displacement parameters, bond lengths, and valence angles are presented in Tables S1–S3 of the Supplementary Material. The lattice parameters obtained from DFT calculations of Eu*RE*CuTe₃ (*RE* = Ho, Tm, Lu, Sc; Table S4) were in good agreement with the experimentally determined values (Table 1). The compound EuYbCuTe₃ was unable to be obtained using the halide flux method, but since Yb³⁺ lies between Tm³⁺ and Lu³⁺, whose quaternary tellurides crystallize in the structure type of KZrCuS₃, if EuYbCuTe₃ is experimentally obtained by another method, it will also crystallize in this structure type. Based on this assumption, DFT calculations of the crystal structure, phonon spectrum, and elastic properties of EuYbCuTe₃ were carried out in this study. The calculated values of the electronic parameters and volume were in line with the general trend of their variations (Figures 3 and 4).

In the series of quaternary tellurides Eu*RE*CuTe₃, where *RE* = Ho–Lu and Sc, the unit-cell volume decreases from 693.40 to 651.52 Å³ (Table 1, Figure 3), and the unit-cell parameters (*a* = 4.3129–4.2341 Å, *b* = 14.3150–14.1562 Å, *c* = 11.2312–10.8698 Å) decreased, which is consistent with the change in structural parameters as the ionic radius of *RE*³⁺ decreases in the series of Eu*RE*Cu*Ch*₃ chalcogenides (*Ch* = S [22,24], Se [25]), crystallizing in the space group *Cmcm* (Figures 3 and 4). When changing the chalcogenide in the series Te²⁻ \rightarrow Se²⁻ \rightarrow S²⁻, the anion radii decrease by 10% and 7% (r_i (Te²⁻) = 2.21 Å, r_i (Se²⁻) = 1.98 Å, r_i (S²⁻) = 1.84 Å [32]), respectively. As a result, the unit-cell volumes changed by approximately 18% and 12% (Figure 3), and the unit-cell parameters changed by 6% and 4%, respectively (Figure 4).



Figure 3. Relationship between the experimental (shaded shapes) and calculated (unshaded shapes) values of the unit-cell volume as a function of the ionic radius of the rare-earth metal cation in the series of the compounds $EuRECuTe_3$ (RE = Ho [this work], Er [19], Tm [this work], Yb [this work], Lu [20], Sc [this work]), $EuRECuSe_3$ (RE = Er [26], Tm-Lu [25], Sc [18]), and $EuRECuS_3$ (RE = Tm-Lu [22], Sc [8]).



Figure 4. Relationship between the unit-cell parameters (*a*: black, *b*: blue, *c*: red) and the ionic radius of the rare-earth metal cation in the series of compounds Eu*RE*CuTe₃ (*RE* = Ho [this work], Er [19], Tm [this work], Yb [this work], Lu [20], Sc [this work]), Eu*RE*CuSe₃ (*RE* = Er [26], Tm–Lu [25], Sc [18]), and Eu*RE*CuS₃ (*RE* = Tm–Lu [22], Sc [8]).

In the structures of Eu*RE*CuTe₃ (*RE* = Ho, Tm, Sc), four distances d(Cu-Te) are shorter than the theoretical value of 2.81 Å [32] by 5–7%, while the fifth and sixth distances (4.293–4.086 Å) are longer by 45–52% (Figure S1). The typical coordination polyhedron of copper in this structure is a tetrahedron (Figures 5 and S1). The tetrahedra [CuTe₄]^{7–} are linked by shared anions (Te1)^{2–} along the *a*-axis (Figure 5). As the rare-earth metal cation radius decreased in the quaternary tellurides, a decrease in the ionicity of the Cu–Te bond was observed in the tetrahedra, resulting in the bond lengths d(Cu-Te) changing from 2.644 to 2.615 Å and from 2.668 to 2.620 Å (Table S3, Figure 6).



Figure 5. Projection of the crystal structure of the EuRECuTe₃ representatives in the space group Cmcm.

The values of the valence angles \angle (Te–Cu–Te), ranging from 104.4 to 111.0° (Table S3), deviate from the ideal tetrahedral angle by 1–4%. As the compound changed from EuHoCuTe₃ to EuScCuTe₃, this deviation decreases. The reduction in the distortion of $[CuTe_4]^{7-}$ in the series of compounds Eu*RE*CuTe₃ (*RE* = Ho–Lu, Sc) is confirmed by the calculation of the τ_4 descriptor [46], which increases in this series from 0.977 to 0.992 (Figure 7). Since the τ_4 descriptor values for an ideal tetrahedron, trigonal pyramid, square pyramid, and ideal square are 1.00, 0.85, 0.64–0.07, and 0.00, respectively [46], in the structures of Eu*RE*CuTe₃, a distortion of the copper coordination polyhedron from an ideal tetrahedron to a trigonal pyramid is observed at 2.3–0.8%. The scandium telluride possesses an almost ideal tetrahedral coordination environment. The degree of distortion of the tetrahedral [Cu*Ch*₄]^{7–} polyhedra (*Ch* = Se, Te) in the tellurides Eu*RE*CuTe₃ was found to be higher than in the selenides Eu*RE*CuSe₃ (Figure 7).



Figure 6. The distance d(M–Te) in the structures of Eu*RE*CuTe₃ compounds with M = Eu, Cu, *RE* (= Ho [this work], Er [19], Tm [this work], Lu [20], and Sc [this work]).



Figure 7. Calculated values of the τ_4 descriptor for the polyhedra $[CuCh_4]^{7-}$ (*Ch* = Se, Te) in the structures of the compounds Eu*RE*CuTe₃ (*RE* = Ho [this work], Er [19], Tm [this work], Yb [this work], Lu [20], Sc [this work]) and Eu*RE*CuSe₃ (*RE* = Er [26], Tm–Lu [25], Sc [18]) in the space group *Cmcm*.

In the structures of the Eu*RE*CuTe₃ compounds in the space group *Cmcm*, the distances d(RE-Te) (Table S3) deviate from theoretical values (2.96 Å (EuScCuTe₃)–3.11 Å (EuHoCuTe₃) [32]) by 1–2%. The coordination polyhedra of RE^{3+} in the structures of Eu*RE*CuTe₃ (RE = Ho, Tm, Sc) are octahedra, which show distortions. The valence angles \angle (Te–RE-Te), ranging from 86.3 to 93.7° (Table S3), deviate from the ideal octahedral angle by 4%. The octahedral units [$RETe_6$]^{9–} are connected to each other through (Te1)^{2–} anions along the *c*-axis and through (Te2)^{2–} anions along the *a*-axis (Figure 5). The coordination polyhedra [$RETe_6$]^{9–} and [$CuTe_4$]^{7–} share common anions (Se1)^{2–} and (Se2)^{2–} and form two-dimensional layers in the *ac*-plane. In the octahedron, as the radius of RE^{3+} decreases, there is a reduction in the bond lengths d(RE-Te) from 3.0368 to 2.9334 Å and from 3.0501 to 2.9449 Å (Table S3, Figure 6), leading to a crystal-chemical compression of the two-dimensional layers [$RECuTe_3$]^{2–}.

The anions $(Te2)^{2-}$ and $(Te1)^{2-}$ form trigonal prisms $[EuTe_6]^{10-}$ around the Eu^{2+} cations (Figure S1) connected to each other along the *a*-axis. The length of the four bonds d(Eu-Te2) in the structures range from 3.3468 to 3.3491 Å, while the lengths of the other two bonds d(Eu-Te1) are between 3.292 and 3.2961 Å (Figure 6, Table S3). Six distances d(Eu-Te) deviate from the theoretical value of 3.38 Å [32] by 2.5–2.6%, while the seventh and eighth distances (3.877–3.706 Å) are longer by 9.6–14.7% (Figure S1). The sums of valence efforts for the compounds $EuRECuTe_3$ (RE = Ho–Lu and Sc) taking coordination into account are Eu (1.63–1.65), *RE* (2.66–3.09), and Cu (1.33–1.57) (Table S5).

The crystal structure of compounds $EuRECuTe_3$ (RE = Ho-Lu, Sc) is formed by parallel two-dimensional layers in the *ac*-plane, consisting of octahedra and tetrahedra, which are separated by one-dimensional chains of trigonal prisms (Figure 5).

3.2. Band Structure

The path in the Brillouin zone of the space group *Cmcm* is $\Gamma(0,0,0)$, $\Upsilon(^{1}/_{2},^{1}/_{2},0)$, $\Upsilon(^{1}/_{2},^{1}/_{2},0)$, $\Upsilon(^{1}/_{2},^{1}/_{2},0)$, $\Upsilon(^{1}/_{2},^{1}/_{2},0)$. The band structure (Figures 8 and 9) does not include the 4f states of europium and RE^{3+} , since they are replaced by pseudopotentials. As can be seen from the figures, copper and tellurium orbitals provide the main contribution to states near the top of the VB. Orbitals of RE^{3+} (Sc³⁺) and europium provide the main

contribution to the bottom of the CB. Calculations predicted for Eu*RE*CuTe₃ (*RE* = Ho, Tm, Yb, Lu) the indirect band gap Γ -Y. The value of the band gap (1.7–1.8 eV) was a HOMO–LUMO estimation (Table 2). This value is close to experimental data for selenides (EuErCuSe₃ 1.79 eV [26]). For EuScCuTe₃, the calculation predicted a smaller gap, equal to 1.2 eV.



Figure 8. Band structure of EuTmCuTe₃.



Figure 9. Band structure of EuScCuTe₃.

Crystal	Indirect (Γ-Υ)	Crystal	Indirect (Γ–Υ)	Crystal	Indirect (Γ–Υ)
EuHoCuTe ₃	1.72	EuYbCuTe ₃	1.79	EuLuCuTe ₃	1.81
EuTmCuTe ₃	1.77	EuErCuTe ₃	1.75 [19]	EuScCuTe ₃	1.19

Table 2. Calculated band gaps of the tellurides EuRECuTe₃ (RE = Ho–Lu and Sc) in eV.

3.3. Elastic Constants and Elastic Modulus

The elastic constants and elastic modulus of the compound $EuRECuTe_3$ (RE = Ho, Tm, Yb, Lu, Sc) are presented in Table 3. The table presents the bulk module (B), shear module (G), Young's module (Y), and Poisson ratio. These are values for a polycrystal and were calculated by averaging the schemes of Voigt, Reuss, and Hill. The Voigt scheme assumes the uniformity of local strains. The Reuss scheme assumes the uniformity of local strains. The Reuss scheme assumes the uniformity of local strains the upper bound, whereas the Reuss scheme provides the lower bound of value. The approximation of Hill is the average of Voigt and Reuss estimations [47]. The Voigt and Reuss estimates were found to be very different (Table 3), which indicates anisotropy of the elastic properties. The dependence of Young's modulus on direction also illustrates the strong anisotropy of elastic properties (Figure 10).

$$A^{U} = 5 \cdot \frac{G^{V}}{G^{R}} + \frac{B^{V}}{B^{R}} - 6 \tag{1}$$

Table 3. Calculated elastic constants and modulus, as well as Vickers hardness (GPa) of the Eu*RE*CuTe₃ series (*RE* = Ho, Tm, Yb, Lu, and Sc).

RE	C ₁₁	C ₁₂	C ₁₃	C ₂₂	C ₂₃	C ₃₃	C ₄₄	C ₅₅	C ₆₆	Averaging Scheme	В	G	Ŷ	Poisson Ratio	H_V	A^{U}
										Voigt	67	30	77	0.308		
Ho	121	52	40	94	47	113	9	31	45	Reuss	67	21	58	0.356	3.0	1.94
										Hill	67	25	68	0.332		
										Voigt	68	30	79	0.306		
Tm	121	52	40	96	48	114	11	31	45	Reuss	68	24	64	0.343	3.3	1.40
										Hill	68	27	71	0.324		
										Voigt	68	30	79	0.305		
Yb	122	52	40	96	47	114	11	31	45	Reuss	68	24	64	0.342	3.4	1.37
										Hill	68	27	72	0.323		
										Voigt	68	31	80	0.305		
Lu	122	52	40	97	48	115	12	31	45	Reuss	68	24	65	0.339	3.4	1.27
										Hill	68	27	73	0.322		
										Voigt	73	33	86	0.304		
Sc	127	59	42	103	50	127	18	33	45	Reuss	73	29	78	0.322	4.0	0.61
										Hill	73	31	82	0.313		

We also calculated the universal elastic anisotropy index (1). The closer to zero this index is, the lower the anisotropy of elastic properties [48]. By the lanthanoid pressure, at the row $EuRECuTe_3$ (RE = Ho-Lu), anisotropy decreases (Table 3).

$$H_V = 0.92 \left(\frac{G}{B}\right)^{1.137} G^{0.708}$$
(2)

The empirical Formula (2) was used to calculate hardness. According to [49], the formula is based on correlations between Vickers hardness (H_V) and the ratio of shear and bulk moduli. The parameters of the formula were determined from reproducing the hardness of more than forty compounds with ionic and covalent bonds [49]. The shear (G) and bulk (B) modulus in (2) is according to the Hill estimate.



EuHoCuTe₃

EuScCuTe₃

Figure 10. Young's modulus (GPa). Dependence of the direction in the crystals EuHoCuTe₃ and EuScCuTe_{3.}

3.4. Raman, IR, and Phonon Spectra

From the DFT calculation, the wavenumbers and types of modes were determined (Tables 4 and 5). The displacement vectors were obtained from the calculations also. This made it possible to evaluate the participation of each ion in a particular mode. The values of ion displacements characterized their participation in the mode (Figures 11 and 12). According to calculations, the phonon spectrum of the crystals $EuRECuTe_3$ (RE = Ho, Tm, Yb, Lu) at the gamma point lay in the frequency range up to 160 cm⁻¹ (Table 4, Figure 11). In this frequency range, not only were light copper ions involved, but also telluride anions and RE^{3+} cations (Figures 11 and 12). The phonon spectrum of the crystals $EuScCuTe_3$ at the gamma point lay in the frequency range up to 230 cm⁻¹ (Figure 12, Table 5). This corresponded to the fact that the mass of scandium is less than that of the other RE^{3+} cations. IR, Raman, and «silent» modes for all crystals are presented in Tables S6–S8.

A strong mixing of vibrations of structural units in crystals EuRECuTe₃ can be noted. In all compounds, the europium ions participated in the frequency range up to \approx 95 cm⁻¹. Calculations predicted a gap in the phonon spectrum in the region \approx 92–110 cm⁻¹ for EuRECuTe₃ (Figure 11). Note that a similar gap was practically absent in the crystal EuScCuTe₃ (Figure 12).

Calculations predicted that in crystals $EuRECuTe_3$ (RE = Ho, Tm, Yb, Lu), the most intense Raman mode has a frequency of about 146 cm⁻¹ (A_{1g}), and the most intense infrared mode has a frequency of about 123 cm⁻¹ (B_{2u}). At the crystal EuScCuTe₃, the most intense Raman mode has a frequency of about 172 cm⁻¹ (B_{2g}), and the most intense infrared modes has a frequency of about 125 cm⁻¹ (B_{2u}). These modes are illustrated in Figures 13 and 14. The calculated Raman spectrum for all crystals is shown in Figure 15. The results of calculating the phonon spectrum can be useful for interpreting IR and Raman spectra of rare-earth metal tellurides $EuRECuTe_3$. The IR and Raman spectra of $EuRECuTe_3$ (RE = Ho, Tm, Lu) obtained from calculations are similar to the spectra of $EuErCuTe_3$ [19]. It can be assumed that the experimental spectra of $EuErCuTe_3$ (RE = Ho, Tm, Lu) will be similar to the previously presented experimental spectrum of $EuErCuTe_3$ [19].

		Ι	R	R	aman		
cm ⁻¹	Туре	Active/Inactive	Intensity IR (km∙mol ^{−1})	Active/Inactive	Intensity Raman (Arbitrary Units)	Involved Ions ¹	
35	B _{1u}	А	8.5	Ι		Eu ^S , Yb ^S , Cu ^W , Te1 ^S , Te2 ^S	
49	Au	Ι	0	Ι		Yb ^S , Te2 ^S	
53	B _{1g}	Ι	0	А	384	Eu ^S , Cu ^S , Te1 ^S , Te2 ^W	
60	Ag	Ι	0	А	576	Eu ^S , Cu ^S , Te1 ^S , Te2	
62	B_{2g}	Ι	0	А	330	Eu ^S , Cu ^W , Te2	
66	B_{2u}	А	10.5	Ι		Eu, Yb ^S , Cu ^S , Te1 ^S , Te2 ^W	
69	B _{1u}	А	10.3	Ι		Eu ^W , Yb ^S , Cu ^S , Te1, Te2	
79	B_{2g}	Ι	0	А	346	Eu, Cu ^S , Te2	
82	B _{3u}	А	39.1	Ι		Eu, Yb, Cu ^S , Te1 ^W , Te2	
85	B_{1g}	Ι	0	А	218	Eu ^S , Cu ^S , Te1, Te2	
86	Ag	Ι	0	А	138	Eu ^S , Cu ^S , Te2	
87.87	B_{1u}	А	88.2	Ι		Eu ^S , Yb, Cu ^S , Te2	
88.48	B _{2u}	А	0.4	Ι		Eu ^S , Yb, Cu ^S , Te1 ^W	
92	B _{3u}	А	128.3	Ι		Eu ^S , Yb, Cu ^W , Te1 ^W , Te2	
110	B _{3u}	А	13.5	Ι		Eu ^W , Yb ^S , Cu ^S , Te1	
112	B_{3g}	Ι	0	А	133	Te2 ^S	
117	Au	Ι	0	Ι		Yb, Te2	
118.56	B _{1u}	А	390.4	Ι		Yb, Cu ^S , Te1 ^W , Te2	
118.83	B_{1g}	Ι	0	А	37	Eu, Cu, Te1 ^W , Te2 ^S	
122	B _{2g}	Ι	0	А	0.00	Eu, Cu, Te1, Te2	
123	B _{2u}	А	529.2	Ι		Eu, Yb, Te2	
131.52	B_{1g}	Ι	0	А	43	Eu, Cu ^S , Te1 ^S	
132.12	B _{3u}	А	78.8	Ι		Eu ^W , Yb ^W , Cu ^W , Te1 ^S , Te2	
132.17	B _{2u}	А	83.2	Ι		Eu ^W , Cu ^S , Te1 ^S	
132.34	Ag	Ι	0	А	93	Eu, Te1, Te2	
138	Ag	Ι	0	А	62	Cu ^S , Te1, Te2 ^W	
143	B _{2g}	Ι	0	А	174	Eu ^W , Cu ^S , Te1, Te2	
146	Ag	Ι	0	А	1000	Cu, Te1, Te2	
147	B _{1u}	А	0.4	Ι		Yb, Cu, Te2	
149	B _{2g}	Ι	0	А	25	Cu, Te1 ^S , Te2	
153	B _{1u}	А	111.2	Ι		Yb, Cu, Te1 ^S , Te2 ^W	
153	B _{3u}	А	170.4	Ι		Yb, Cu, Te2	
158	B _{3u}	А	10.2	Ι		Yb, Cu ^S , Te1, Te2 ^W	

Table 4. Phonons at the gamma point of EuYbCuTe₃.

¹ Superscripts "S" and "W" denote strong and weak ion displacements in the mode, respectively.

Table 5. Phonons at the gamma point of EuScCuTe₃.

		I	R	R	aman	
Frequency, cm ⁻¹	Туре	Active/Inactive	Intensity IR (km∙mol ^{−1})	Active/Inactive	Intensity Raman (Arbitrary Units)	Involved Ions ¹
46	B _{1u}	А	0	Ι		Eu ^S , Sc ^S , Cu ^W , Te1 ^S , Te2 ^S
53	B_{1g}	Ι	0	А	0.00	Eu ^S , Cu ^S , Te1 ^S , Te2 ^W
57	B_{2u}	А	13.9	Ι		Sc ^S , Cu ^S , Te1 ^S , Te2
58.23	B _{1u}	А	20.3	Ι		Sc ^S , Cu ^S , Te1 ^S , Te2 ^S
58.30	Au	Ι	0	Ι		Sc ^S , Te2 ^S
61	Ag	Ι	0	А	0.00	Eu ^S , Cu ^S , Te1 ^S , Te2
71	B_{2g}	Ι	0	А	896.00	Eu ^S , Cu ^S , Te2
76	B_{2g}	Ι	0	А	0.31	Eu ^S , Cu ^S , Te2
81	B_{1g}	Ι	0	А	0.00	Eu ^S , Cu ^S , Te1, Te2
86	A_g^o	Ι	0	А	0.00	Eu ^S , Cu ^S , Te1 ^W , Te2
89	B _{3u}	А	142.4	Ι		Eu ^S , Sc, Cu ^S , Te1 ^W , Te2
94	B _{1u}	А	192.2	Ι		Eu ^S , Sc, Cu, Te2

		I	R	R	aman	
rrequency, cm ⁻¹	Туре	Active/Inactive	Intensity IR (km∙mol ^{−1})	Active/Inactive	Intensity Raman (Arbitrary Units)	Involved Ions ¹
96	B _{3u}	А	122.4	Ι		Eu, Sc, Cu, Te1 ^W , Te2
98	B _{2u}	А	0.01	Ι		Eu ^S , Sc ^S , Cu, Te1 ^W , Te2 ^W
106	B_{3g}	Ι	0	А	0.00	Te2 ^S
118	B_{1g}	Ι	0	А	0.00	Eu, Cu ^W , Te2
119	B_{2g}	Ι	0	А	89.31	Eu ^W , Cu ^W , Te1 ^S , Te2
122	Au	Ι	0	Ι		Sc ^S , Te2
125	B _{2u}	А	1388.7	Ι		Eu ^W , Sc ^S , Te2
137	Ag	Ι	0	А	0.00	Eu ^W , Te1 ^W , Te2
141	B _{3u}	А	30.2	Ι		Eu ^W , Te1 ^S , Te2
149	B _{2g}	Ι	0	А	41.83	Eu ^W , Cu ^W , Te1 ^S , Te2
150	B_{1u}	А	1108.3	Ι		Sc ^S , Cu, Te1, Te2 ^W
153	Ag	Ι	0	А	0.00	Te1 ^S , Te2
155	B _{3u}	А	5.3	Ι		Sc ^S , Cu ^S , Te1 ^W , Te2 ^W
167.18	B _{1u}	А	96.4	Ι		Sc, Cu ^S , Te1, Te2
167.26	Ag	Ι	0	А	0.00	Cu ^S , Te1 ^W , Te2
169	B_{2u}	А	131.6	Ι		Sc ^W , Cu ^S , Te1
170	B_{1g}	Ι	0	А	0.00	Cu ^S , Te1
172	B_{2g}	Ι	0	А	1000.00	Cu ^S , Te2
207	B_{1u}	А	0.5	Ι		Sc ^S , Cu ^W , Te2 ^W
210	B _{3u}	А	33.6	Ι		Sc ^S , Cu ^W , Te2 ^W
225	B _{3u}	А	276.5	Ι		Sc ^S , Cu ^W

Table 5. Cont.

¹ Superscripts "S" and "W" denote strong and weak ion displacements in the mode, respectively.



Figure 11. The values of ion displacements at phonon modes in EuYbCuTe₃ (space group: *Cmcm*).



Figure 12. The values of ion displacements at phonon modes in EuScCuTe₃ (space group: *Cmcm*).



Figure 13. Ion displacements in IR and Raman modes with maximum intensity at EuYbCuTe₃.

The largest ion displacement was 0.040 Å (Cu). In the case when the displacement was greater than or equal to 0.02 Å, the displacement is indicated by "S". If the displacement did not exceed 0.01 Å, then the displacement is indicated by "W". If the value of displacement was less than 0.005 Å, then the ion is not mentioned in the column "participants".

The largest ion displacement is 0.05 Å (Sc). In the case when the displacement was greater than or equal to 0.02 Å, the displacement is indicated by "S". If the displacement did not exceed 0.01 Å, then the displacement is indicated by "W". If the value of displacement was less than 0.005 Å, then the ion is not mentioned in the column "participants".



Figure 14. Ion displacements in IR and Raman modes with maximum intensity at EuScCuTe₃.



Figure 15. The simulated Raman spectra. The calculation was carried out for the exciting laser wavelength λ = 532 nm and *T* = 300 K. When modelling the Raman spectra based on the calculated wavenumbers and intensities, the functions pseudo-Voigt with dumping factor 8 cm⁻¹ were used.

4. Conclusions

Single crystals of layered heterometallic tellurides $EuRECuTe_3$ (RE = Ho, Tm, and Sc) were synthesized for the first time. The orthorhombic compounds crystallized in the space group *Cmcm*. With a decrease in the parameters and volume of the unit cell, the bond length d(RE-Te) occurred as the ionic radius of the rare-earth metal cation decreases ($RE^{3+} = Ho^{3+}$, Er^{3+} , Tm^{3+} , Yb^{3+} , Lu^{3+} , Sc^{3+}), leading to a crystal-chemical compression of the two-dimensional layers in the crystal structures of the $EuRECuTe_3$ compounds. The patterns of changes in structural parameters were compared with the isostructural chalcogenides $EuRECuCh_3$ (Ch = S, Se, Te) in the space group *Cmcm*. In the series of chalcogenides, the degree of distortion of the copper coordination polyhedra was found

to be highest in the tellurides. Within the framework of the DFT approach, by using the hybrid functional, which takes into account non-local HF exchange, the crystal structure and IR, Raman, and "silent" modes were studied. Elastic tensor as well as elastic moduli and hardness were calculated. The theoretical calculations allow for the assignment of vibrational modes as well as revealing the involved ions that participated in these modes.

Supplementary Materials: The following Supporting Information can be downloaded at: https:// www.mdpi.com/article/10.3390/ma17143378/s1, Figure S1. Coordination polyhedra of [CuTe₄]^{7–} (left), [EuTe₆]^{10–} (right) in Eu*RE*CuTe₃ (*RE* = Ho (this work), Er [19], Tm (this work), Lu [20], Sc (this work) from top to bottom). Table S1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of the Eu*RE*CuTe₃ (*RE* = Ho, Tm, Sc) samples. Table S2. Atomic displacement parameters (Å²) of the Eu*RE*CuTe₃ (*RE* = Ho, Tm, Sc) samples. Table S3. Bond lengths (d / Å) and angles ($\angle / °$) in the crystal structures of the Eu*RE*CuTe₃ representatives with *RE* = Ho, Tm and Sc. Table S4. Unit-cell parameters obtained by DFT methods. Table S5. Bond-valence calculation data for the Eu*RE*CuTe₃ representatives with *RE* = Ho, Tm, Yb, Lu and Sc. Table S7. Calculated Raman modes of the Eu*RE*CuTe₃ representatives with *RE* = Ho, Tm, Yb, Lu and Sc. Table S8. Calculated "silent" modes of the Eu*RE*CuTe₃ representatives with *RE* = Ho, Tm, Yb, Lu and Sc.

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References

- 1. Ishtiyak, M.; Jana, S.; Karthikeyan, R.; Mamindla, R.; Tripathy, B.; Malladi, S.K.; Niranjan, M.; Prakash, J. Syntheses of five new layered quaternary chalcogenides SrScCuSe₃, SrScCuTe₃, BaScCuSe₃, BaScCuTe₃, and BaScAgTe₃: Crystal structures, thermoelectric properties, and electronic structures. *Inorg. Chem. Front.* **2021**, *8*, 4086–4101. [CrossRef]
- Pal, K.; Xia, Y.; Shen, J.; He, J.; Luo, Y.; Kanatzidis, M.G.; Wolverton, C. Accelerated discovery of a large family of quaternary chalcogenides with very low lattice thermal conductivity. *Comput. Mater.* 2021, 7, 82. [CrossRef]
- 3. Pal, K.; Xia, Y.; He, J.; Wolverton, C. High thermoelectric performance in BaAgYTe₃ via low lattice thermal conductivity induced by bonding heterogeneity. *Phys. Rev. Mater.* **2019**, *3*, 085402. [CrossRef]
- 4. Pal, K.; Hua, X.; Xia, Y.; Wolverton, C. Unraveling the structure-valence-property relationships in *AMM'Q*₃ chalcogenides with promising thermoelectric performance. *ACS Appl. Energy Mater.* **2019**, *3*, 2110–2119. [CrossRef]
- Babo, J.-M.; Choi, E.S.; Albrecht-Schmitt, T.E. Synthesis, structure, magnetism, and optical properties of Cs₂Cu₃DyTe₄. *Inorg. Chem.* 2012, *51*, 11730–11735. [CrossRef]
- 6. Meng, C.-Y.; Chen, H.; Wan, P.; Chen, L. Syntheses, Structures, and Magnetic and Thermoelectric Properties of Double-Tunnel Tellurides: *A*_x*RE*₂Cu_{6-x}Te₆ (*A* = K–Cs; *RE* = La–Nd). *Chem. Mater.* **2011**, *23*, 4910–4919. [CrossRef]
- Pavlyuk, M.D. Detector Crystals Based on CdTe and Cd_{1-x}Zn_xTe for Direct Detection of X-ray and Gamma Quanta. Ph.D. Thesis, A.V. Shubnikov Institute of Crystallography RAS, Moscow, Russia, 25 August 2020.
- Ruseikina, A.V.; Molokeev, M.S.; Chernyshev, V.A.; Aleksandrovsky, A.S.; Krylov, A.S.; Krylova, S.N.; Velikanov, D.A.; Grigoriev, M.V.; Maximov, N.G.; Shestakov, N.P.; et al. Synthesis, structure, and properties of EuScCuS₃ and SrScCuS₃. *J. Solid State Chem.* 2021, 296, 121926. [CrossRef]
- Ishtiyak, M.; Jana, S.; Panigrahi, G.; Srivastava, A.K.; Narayanswamy, S.; Bhattacharjee, P.P.; Niranjan, M.K.; Prakash, J. Syntheses, crystal structures, optical, and theoretical study of two ternary chalcogenides CsSc₅Te₈ and Cs_{0.6(1)}Ti₆Se₈ with tunnel structures. *Solid State Sci.* 2021, 114, 106577. [CrossRef]

- Chen, L.; Corbett, J.D. Synthesis, Structure, and Bonding of Sc₆MTe₂ (*M* = Ag, Cu, Cd): Heterometal-Induced Polymerization of Metal Chains in Sc₂Te. *Inorg. Chem.* 2002, *41*, 2146–2150. [CrossRef]
- Ishtiyak, M.; Panigrahi, G.; Jana, S.; Prakash, J.; Mesbah, A.; Malliakas, C.D.; Lebègue, S.; Ibers, J.A. Modulated Linear Tellurium Chains in Ba₃ScTe₅: Synthesis, Crystal Structure, Optical and Resistivity Studies, and Electronic Structure. *Inorg. Chem.* 2020, 59, 2434–2442. [CrossRef]
- 12. Ruseikina, A.V.; Grigoriev, M.V.; Molokeev, M.S.; Garmonov, A.A.; Elyshev, A.V.; Locke, R.J.C.; Schleid, Th. Synthesis, Crystal Structure and Properties of the New Laminar Quaternary Tellurides Sr*Ln*CuTe₃ (*Ln* = Sm, Gd–Tm and Lu). *Crystals* **2023**, *13*, 291. [CrossRef]
- Babo, J.-M.; Albrecht-Schmitt, T.E. Ce₂AgYb_{5/3}Se₆, La₂CuErTe₅, and Ce₂CuTmTe₅: Three new quaternary interlanthanide chalcogenides. *J. Solid State Chem.* 2013, 197, 414–419. [CrossRef]
- Huang, F.Q.; Ibers, J.A. Syntheses, Structures, and Theoretical Study of LaCuSTe and SmCuSTe. *Inorg. Chem.* 1999, 38, 5978–5983. [CrossRef] [PubMed]
- 15. Babo, J.M.; Schleid, Th. CsCu₂Sc₃Te₆ and CsCuY₂Te₄: Two new quaternary cesium copper rare-earth metal tellurides. *Solid State Sci.* **2010**, *12*, 238–245. [CrossRef]
- Koscielski, L.A.; Ibers, J.A. The structural chemistry of quaternary chalcogenides of the type AMM'Q₃. Z. Anorg. Allg. Chem. 2012, 638, 2585–2593. [CrossRef]
- 17. Huang, F.Q.; Choe, W.; Lee, S.; Chu, J.S. Syntheses and Crystal Structures of Three Copper Tellurides: BaDyCuTe₃, K_{1.5}Dy₂Cu_{2.5}Te₅, and Acentric K_{0.5}Ba_{0.5}DyCu_{1.5}Te₃. *Chem. Mater.* **1998**, *10*, 1320–1326. [CrossRef]
- Grigoriev, M.V.; Ruseikina, A.V.; Chernyshev, V.A.; Oreshonkov, A.S.; Garmonov, A.A.; Molokeev, M.S.; Locke, R.J.C.; Elyshev, A.V.; Schleid, T. Single Crystals of EuScCuSe₃: Synthesis, Experimental and DFT Investigations. *Materials* 2023, 16, 1555. [CrossRef] [PubMed]
- Ruseikina, A.V.; Grigoriev, M.V.; Locke, R.J.C.; Chernyshev, V.A.; Garmonov, A.A.; Schleid, Th. Synthesis, Crystal Structure, and Optical and Magnetic Properties of the New Quaternary Erbium Telluride EuErCuTe₃: Experiment and Calculation. *Materials* 2024, 17, 2284. [CrossRef] [PubMed]
- 20. Ruseikina, A.V.; Grigoriev, M.V.; Garmonov, A.A.; Molokeev, M.S.; Schleid, Th.; Safin, D.A. Synthesis, structures and magnetic properties of the Eu-based quaternary tellurides EuGdCuTe₃ and EuLuCuTe₃. *Cryst. Eng. Comm.* **2023**, *25*, 1716–1722. [CrossRef]
- Ruseikina, A.V.; Andreev, O.V. Regularities of Change in the Structural Parameters of EuLnCuS₃ (Ln = La–Nd, Sm, Gd, Ho). Russ. J. Inorg. Chem. 2017, 62, 160–167. [CrossRef]
- 22. Wakeshima, M.; Furuuchi, F.; Hinatsu, Y. Crystal structures and magnetic properties of novel rare-earth copper sulfides, EuRCuS₃ (*R* = Y, Gd–Lu). *J. Phys. Condens. Matter.* **2004**, *16*, 5503–5518. [CrossRef]
- Furuuchi, F.; Wakeshima, M.; Hinatsu, Y. Magneticproperties and ¹⁵¹Eu Mo¨ssbauer effects of mixed valence europium copper sulfide, Eu₂CuS₃. J. Solid State Chem. 2004, 177, 3853–3858. [CrossRef]
- Ruseikina, A.V.; Chernyshev, V.A.; Velikanov, D.A.; Aleksandrovsky, A.S.; Shestakov, N.P.; Molokeev, M.S.; Grigoriev, M.V.; Andreev, O.V.; Garmonov, A.A.; Matigorov, A.V.; et al. Regularities of the property changes in the compounds EuLnCuS₃ (*Ln* = La–Lu). *J. Alloys Compd.* 2021, 874, 159968. [CrossRef]
- Grigoriev, M.V.; Solovyov, L.A.; Ruseikina, A.V.; Aleksandrovsky, A.S.; Chernyshev, V.A.; Velikanov, D.A.; Garmonov, A.A.; Molokeev, M.S.; Oreshonkov, A.S.; Shestakov, N.P.; et al. Quaternary Selenides Eu*Ln*CuSe₃: Synthesis, Structures, Properties and In Silico Studies. *Int. J. Mol. Sci.* 2022, 23, 1503. [CrossRef] [PubMed]
- Andreev, O.V.; Atuchin, V.V.; Aleksandrovsky, A.S.; Denisenko, Y.G.; Zakharov, B.A.; Tyutyunnik, A.P.; Habibullayev, N.N.; Velikanov, D.A.; Ulybin, D.A.; Shpindyuk, D.D. Synthesis, structure, and properties of Eu*Ln*CuSe₃ (*Ln* = Nd, Sm, Gd, Er). *Crystals* 2022, 12, 17. [CrossRef]
- 27. Shahid, O.; Ray, A.K.; Yadav, S.; Deepa, M.; Niranjan, M.K.; Prakash, J. Structure-property relationships and DFT studies of three quaternary chalcogenides: BaCeCuSe₃, BaCeAgS₃, and BaCeAgSe₃. *Mater. Res. Bull.* **2023**, *168*, 112469. [CrossRef]
- Shahid, O.; Yadav, S.; Maity, D.; Deepa, M.; Niranjan, M.K.; Prakash, J. Synthesis, crystal structure, DFT, and photovoltaic studies of BaCeCuS₃. New J. Chem. 2023, 47, 5378–5389. [CrossRef]
- 29. Murashko, Y.A.; Ruseikina, A.V.; Kislitsyn, A.A.; Andreev, O.V. Optical and Thermal Properties of the Eu*Ln*CuS₃ (*Ln* = La, Pr, Sm, Gd) Compounds. *Inorg. Mater.* **2015**, *51*, 1213–1218. [CrossRef]
- 30. Yang, Y.; Ibers, J.A. Synthesis and characterization of a series of quaternary chalcogenides Ba*LnMQ*₃ (*Ln* = Rare Earth, *M* = Coinage Metal, *Q* = Se or Te). *J. Solid State Chem.* **1999**, 147, 366–371. [CrossRef]
- 31. Prakash, J.; Mesbah, A.; Beard, J.C.; Ibers, J.A. Syntheses and crystal structures of BaAgTbS₃, BaCuGdTe₃, BaCuTbTe₃, BaAgTbTe₃, and CsAgUTe₃. Z. Anorg. Allg. Chem. **2015**, 641, 1253–1257. [CrossRef]
- 32. Shannon, R.D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr.* **1976**, *A32*, 751–767. [CrossRef]
- 33. Mansuetto, M.F.; Keane, P.M.; Ibers, J.A. Synthesis and Structures of the New Group IV Chalcogenides NaCuTiS₃ and NaCuZrQ₃ (*Q* = S, Se, Te). *J. Solid State Chem.* **1993**, *105*, 580–587. [CrossRef]
- 34. Eberle, M.A.; Schleid, Th. Expanding the SrCu*RES*₃ Series with the Rare-Earth Metals Scandium and Yttrium. *Z. Kristallogr.* **2016**, *S36*, 82.
- 35. Eberle, M.A. Darstellung und Charakterisierung Quaternärer Seltenerdmetall-Verbindungen in Kombination mit Kupfer und Schwefel. Ph.D. Thesis, University of Stuttgart, Stuttgart, Germany, 2016.

- 36. Ruseikina, A.V.; Grigoriev, M.V.; Solovyov, L.A.; Chernyshev, V.A.; Aleksandrovsky, A.S.; Krylov, A.S.; Krylova, S.N.; Shestakov, N.P.; Velikanov, D.A.; Garmonov, A.A.; et al. A Challenge toward Novel Quaternary Sulfides SrLnCuS₃ (*Ln* = La, Nd, Tm): Unraveling Synthetic Pathways, Structures and Properties. *Int. J. Mol. Sci.* 2022, 23, 12438. [CrossRef] [PubMed]
- 37. Azarapin, N.O. Synthesis, Structure and Properties of Compounds BaRECuS₃ (*RE* = Rare-Earth Element). Ph.D. Thesis, University of Tyumen, Tyumen, Russia, 4 October 2022.
- 38. Wu, P.; Christuk, A.E.; Ibers, J.A. New Quaternary Chalcogenides Ba*LnMQ*₃ (*Ln* = Rare Earth or Sc; *M* = Cu, Ag; *Q* = S, Se). II. Structure and Property Variation vs. Rare-Earth Element. *J. Solid State Chem.* **1994**, *110*, 337–344. [CrossRef]
- 39. Ruseikina, A.V.; Pinigina, A.N.; Grigoriev, M.V.; Safin, D.A. Elucidating a Series of the Quaternary Selenides BaRECuSe₃ with a Rich Library of Optical Properties. *Cryst. Growth Des.* **2024**, *24*, 2485–2492. [CrossRef]
- 40. Sheldrick, G.M. A short history of SHELX. Acta Crystallogr. 2008, A64, 112–122. [CrossRef]
- 41. PLATON. A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, 2008.
- 42. Becke, A.D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648–5652. [CrossRef]
- 43. Crystal. Available online: http://www.crystal.unito.it/index.php (accessed on 10 April 2024).
- 44. Energy-Consistent Pseudopotentials of the Stuttgart/Cologne Group. Available online: http://www.tc.uni-koeln.de/PP/clickpse. en.html (accessed on 10 April 2024).
- 45. Towler, M. CRYSTAL Resourses Page. Available online: https://vallico.net/mike_towler/crystal.html (accessed on 10 April 2024).
- 46. Yang, L.; Powell, D.R.; Houser, R.P. Structural variation in copper(I) complexes with pyridylmethylamide ligands: Structural analysis with a new four-coordinate geometry index, *τ*₄. *Dalton Trans.* **2007**, *9*, 955–964. [CrossRef]
- 47. Korabelnikov, D.V.; Zhuravlev, Y.N. Ab initio investigations of the elastic properties of chlorates and perchlorates. *Phys. Solid State* **2016**, *58*, 1166–1171. [CrossRef]
- Ranganathan, S.I.; Ostoja-Starzewski, M. Universal Elastic Anisotropy Index. *Phys. Rev. Let.* 2008, 101, 055504. [CrossRef] [PubMed]
- Tian, Y.; Xu, B.; Zhao, Z. Microscopic theory of hardness and design of novel superhard crystals. *Int. J. Refract. Met. Hard Mater.* 2012, 33, 93–106. [CrossRef]

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